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Semi-Annual Progress Report

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MORPHOLOGICAL STABILITY AND FLUID DYNAMICS OF VAPOR CRYSTAL GROWTH

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The work performed and progress achieved during the report period, December 1984 through May 1985, are as follows:

1. Interfacial Heat and Mass Transfer

Good progress has been made in establishing the capabilities of thermal deflection spectroscopy for measurements of the concentration field about a growing crystal. With the argon ion laser restored to full power and pointing stability, we have tested our theoretical model for the effects of the chopping frequency, the ratio of on- to off-periods and the relative positions of the axes of the pumping and probing beams. Good agreement between experimental and theoretical predictions was obtained. Under the thus derived optimum conditions, we can now routinely detect concentration variations of 0.1 torr of iodine in air with a spatial resolution of 1 mm or less. Most importantly, this high sensitivity can be obtained with a local heating of the vapor by the pumping beam of only 2 ^{o}C or less; i.e. the deformation of the temperature profile by the concentration measurement technique is insignificant.

In addition we have determined the conditions under which small variations of the beam spacing has only negligible influence on the deflection effect. Understanding of these conditions will be important for work to follow, when the scanning of the vapor space for concentration mapping will be performed through windows with unavoidable optical imperfections.

Current work is concerned with the differential holographic recording of the crystal surface morphology and the design of a growth cell that will permit simultaneous conduct of holography and thermal deflection spectroscopy during the growth of iodine crystals from vapors (iodine in inert gas) of various temperatures and concentrations.

2. Interface Kinetics and Morphology

Under this topic we have completed the inclusion of the next-nearest

neighbor interaction into our surface roughness model and applied the resulting formalism to copper, zinc and lead, i.e. to systems for which surface roughening has umambiguously been observed for certain crystal faces but not for others. Our model predictions are in perfect agreement with all experimental findings on these systems. The quantitative evaluation of this statistical model is based on thermodynamic parameters that contain information about the relaxed surface states: the heat of sublimation and the energy of formation of bulk vacancies. To the extent that these entities differ from each other, surface relaxation (to-date ignored in surface roughness treatments) is significant. Whereas our initial treatment has centered on metals (for which unambiguous experimental results are available), a carefull survey of the literature shows that surface relaxation, as revealed by a difference in these two energy parameters, exists in covalent and ionic systems as well. A major publication that summarizes our theoretical work will be undertaken this summer.

Future work will concentrate on experimental studies of the surface roughening transition on the model system CBr_4. We will attempt to study interferometrically changes in the surface morphology as they occur at the onset, and at successive degrees of surface roughening, with increasing growth temperature. In addition, we will quantify the surface roughening transition that we have qualitatively observed to be associated with grain boundaries.

3. Mass Spectroscopy

As pointed out in the preceeding progress report, our mass-spectroscopic studies of the transport of GeSe with GeI_4 strongly suggest that the transport reaction that was postulated for the evaluation of earlier space experiments does not apply. Our findings suggest that the compound $GeSe_2$, that had not been considered in this context before, plays a major role in this system.

Hence, we have investigated the conditions under which $GeSe_2$ can form from GeSe, which was first tested for phase purity. We found, in agreement with earlier phase equilibria studies, that in spite of long reaction times, pure GeSe is stable at the temperatures used in the earlier transport studies. In the presence of iodine (from GeI_4), however, large amounts of $GeSe_2$ are readily formed. The $GeSe_2$, on the other hand, undergoes the reaction

$$GeSe_2(s) = GeSe(v) + 1/2\ Se_2(v) \qquad (1)$$

which is coupled with both postulated transport reactions

$$GeSe(s) + GeI_4(v) = GeI_2(v) + 1/2\ Se_2(v) \qquad (2)$$

and

$$GeSe(s) = GeSe(v) \quad . \qquad (3)$$

This combination can explain why our studies reveal only negligible Se_2 concentrations as compared to the GeSe and GeI_4 concentrations in the vapor: as GeSe forms according to (3), reaction (1), which has a low equilibrium constant to start with, leads to the formation of GeSe(s) at the expense of $Se_2(v)$. Hence, it appears that the vapor transport of GeSe(s) occurs simply through sublimation in the form of GeSe(v). However, considerably more work is required, including some actual transport runs of pure GeSe in inert gases, before we will publish this far reaching claim - which would invalidate all current fluid dynamic interpretations of the transport rates obtained in space.

4. Vapor Transport Experiments and Calculations

During the reporting period we have conducted several transport runs at successively lower filling pressures. The results revealed a systematic increase of the actual transport rate over the predicted rate with decreasing pressure. Further attempts to explain this deviation in terms of a systematic computational or experimental error have failed. The filling pressure gauge has been recalibrated, runs were repeated, and identical results were ob-

tained. As a fringe benefit of these clarification efforts we found that transport calculations based on (locally varying) temperature dependent physical properties can yield twice the rates predicted with the conventional average temperature approach, even if the temperature difference between source and crystal is only 20 ^{o}C! Though this is a practically most important finding, it can still not account for the observed differences between model predictions and experiments. Further efforts will concentrate on the influence of thermal diffusion on the model transport rates.

5. Recent Publications and Presentations of NASA-Sponsored Research

Publications

C. Smutek, P. Bontoux, B. Roux, G. H. Schiroky, A. C. Hurford, F. Rosenberger and G. de Vahl Davis: Three-Dimensional Convection in Horizontal Cylinders: Numerical Solutions and Comparison with Experimental and Analytical Results. Numerical Heat Transfer (in press).

P. Bontoux, B. Roux, G. H. Schiroky, B. Markham and F. Rosenberger: Analytical and Two-Dimensional Approximations for Convection in the Vertical Midplane of a Horizontal Cylinder. Int J. Heat Mass Transfer (accepted).

Oral Presentation

J.-S. Chen and F. Rosenberger: Surface Roughening and Rapid Growth as Precursor to a Solid-Solid Phase Transition, accepted for presentation at the Eigth AACG-West Conference on Crystal Growth, June 4-7, 1985, Stanford Sierra Camp, Fallen Leaf Lake, CA.

Recognition

Discussion Leader, Session on Crystal Growth, Gordon Research Conference on Gravitational Effects in Materials, Separation Processes and Living Systems, August 19-23, 1985, Colby-Sawyer College, NH.